Electronic Supplementary Information (ESI)

Novel Ternary Zintl Phosphide Halides Ba_3P_5X (*X* = Cl, Br) with 1D Helical Phosphorus Chains: Synthesis, Crystal and Electronic Structure

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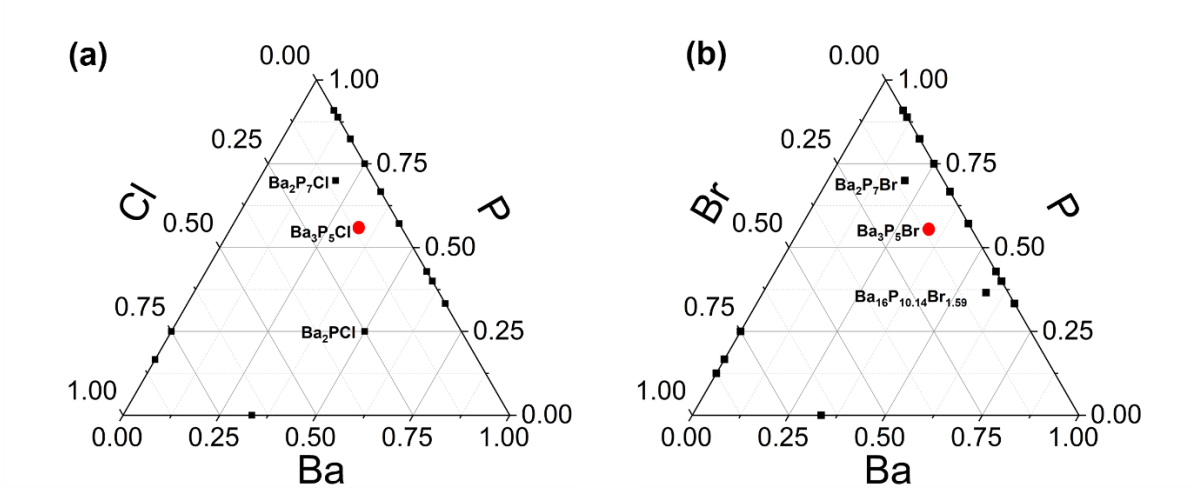

Fig. S1 Compositional diagrams of ternary systems Ba–P–Cl (a) and Ba–P–Br (b). The novel phases Ba_3P_5Cl and Ba_3P_5Br are marked as red circles in (a) and (b). In each compositional diagram, the reported ternary compounds are displayed with black squares, while reported binary compounds are marked as black squares.

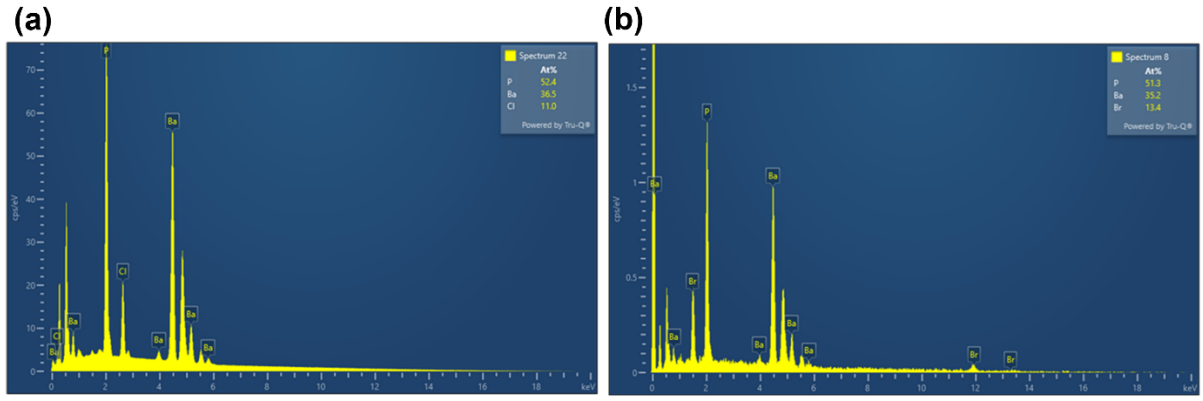

Fig. S2 Representative EDS spectra of Ba_3P_5Cl (a) and Ba_3P_5Br (b).

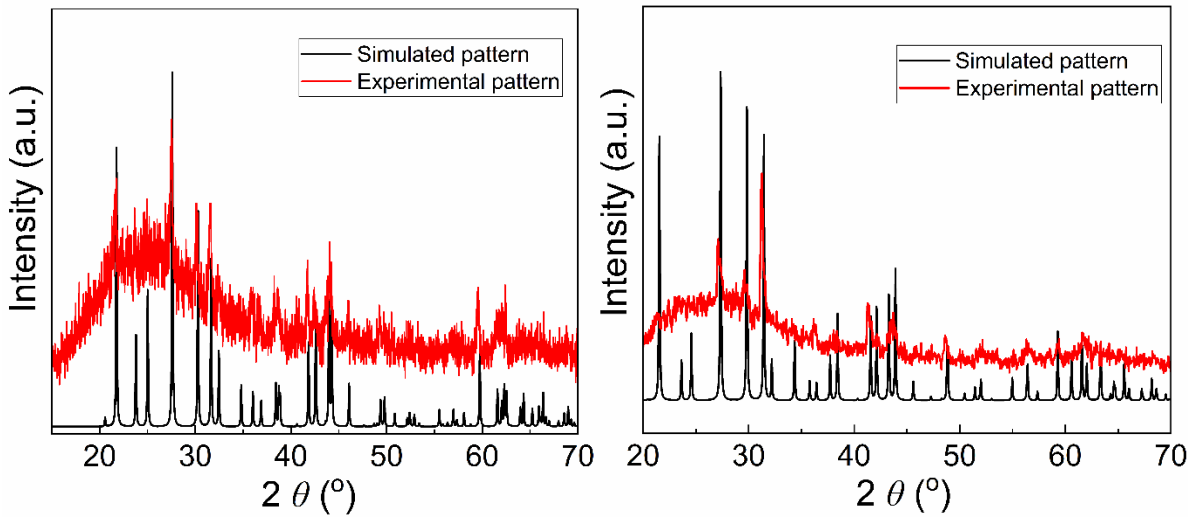

Fig S3. Powder X-ray diffraction patterns of representative Ba_3P_5Cl (left) and Ba_3P_5Br (right) samples. The polycrystalline material was prepared in the glovebox by grinding flux-grown crystals.

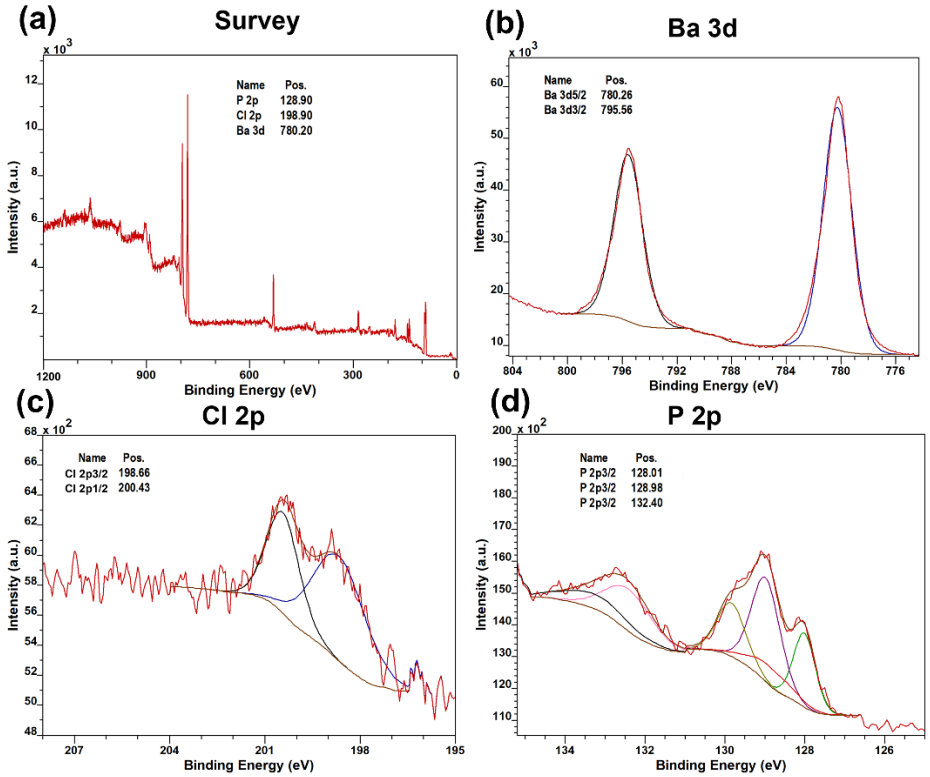

Fig. S4 (a) XPS survey spectrum of polycrystalline Ba_3P_5Cl sample. The high-resolution spectra of (b) Ba 3d, (c) Cl 2p and (d) P 2p.

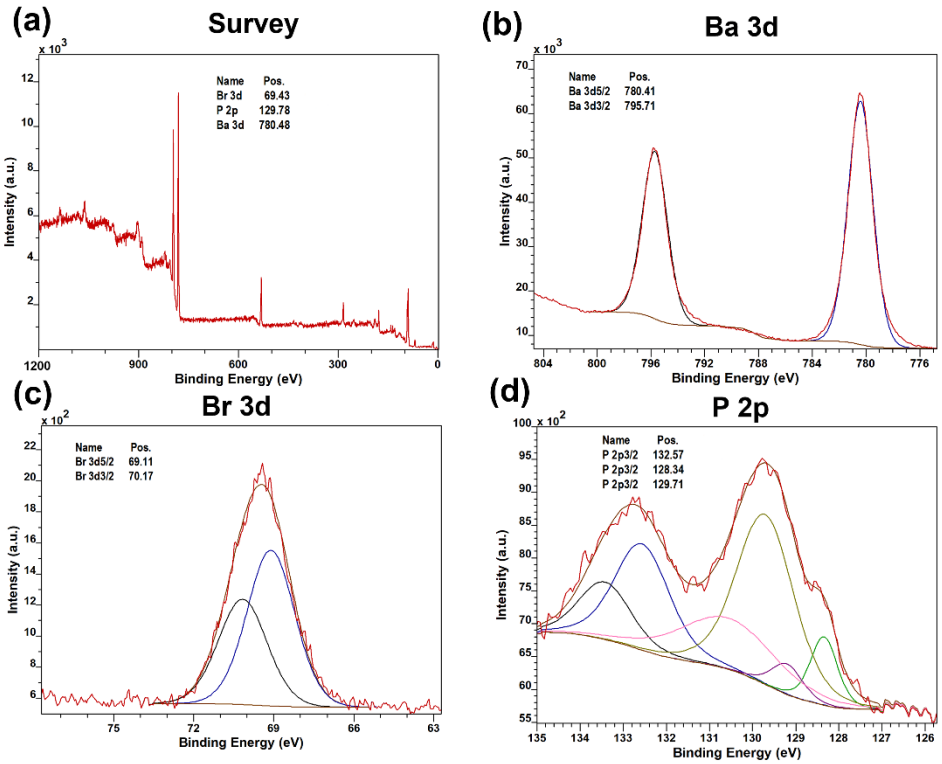

Fig. S5 (a) XPS survey spectrum of polycrystalline Ba_3P_5Br sample. The high-resolution spectra of (b) Ba 3d, (c) Br 3d and (d) P 2p.

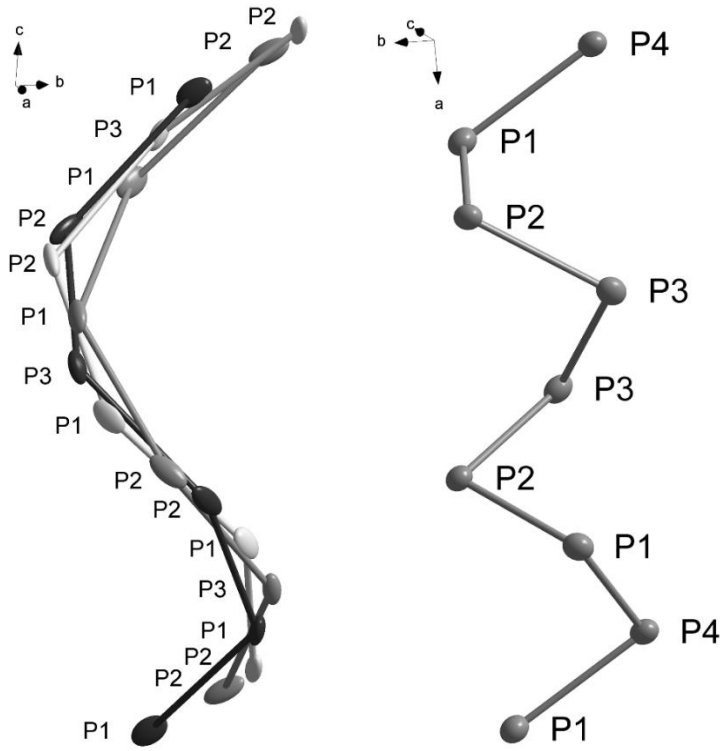

Fig S6. (Left) Propagation of the $^{1}_{\infty}$[P] infinite chain along *c*-axis. The disordered helix is represented as a superposition of three symmetry copies of the same ordered chain sequenced to the {P1—P1—P2—P3—P2} fragment. Three three chains are colored as black, dark gray, and light gray. (Right) The representations of the $^{1}_{\infty}$[P] infinite chain in SnPI.

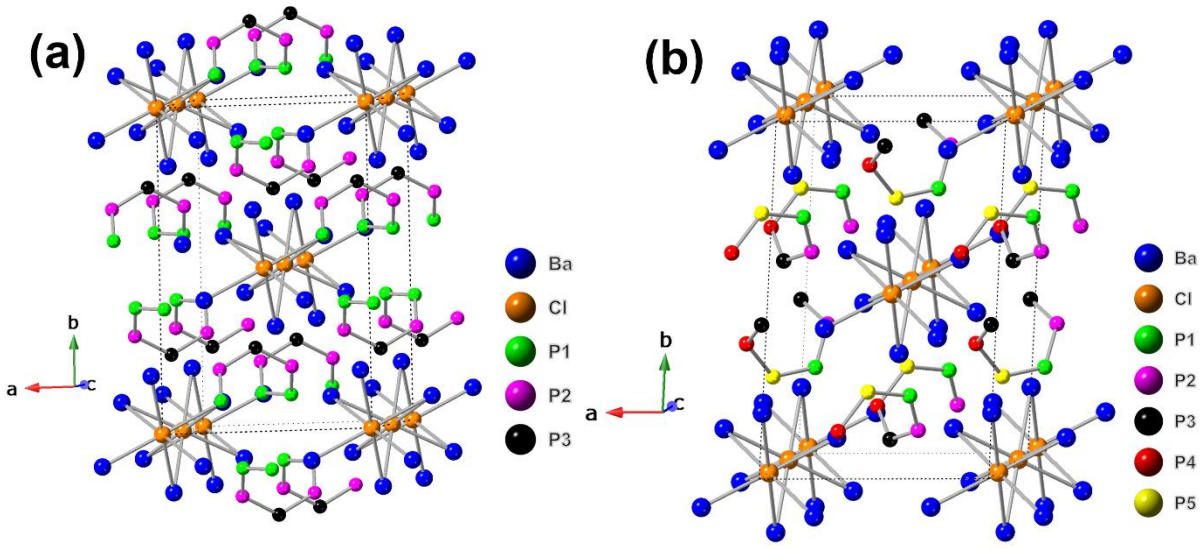

Fig S7. (a) and (b) depict unit cell view of the Ba_3P_5Cl model in space groups *C*2/*c* and *Cc*, respectively, approximately along the *c*-direction. Note, that all atoms are fully occupied.

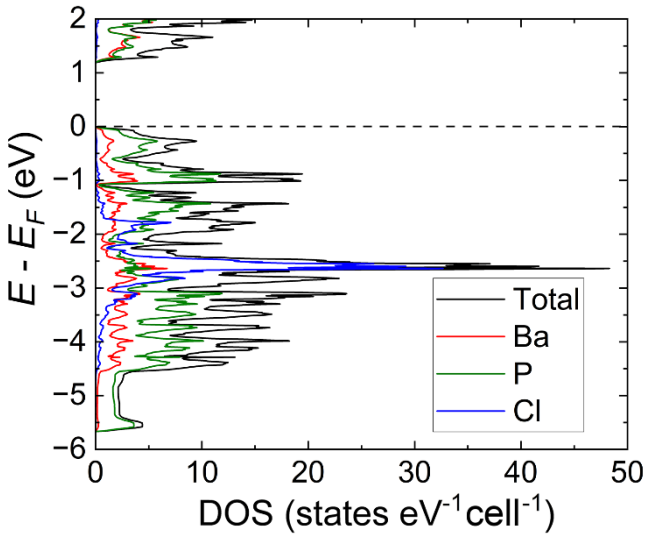

Fig S8. Total (black trace) and projected density of states for the atoms Ba (red trace), P (green trace), and Cl (blue trace) for Ba_3P_5Cl model (Space group = *Cc*). The dashed line at 0 eV shows the Fermi level as a point of reference.

Table S1 Unit cell parameters of Ba_3P_5X (X = Cl, Br) and Ba_3P_5Cl in space group *C*2/*c* and *Cc*, respectively obtained from ISODISTORT program suite and used for the electronic structure calculations.

Lattice parameters	Ba_3P_5Cl	Ba_3P_5Br
Space group	*C*2/*c* and *Cc*	*C*2/*c*
a/(Å)	9.9393	10.0348
b/(Å)	14.9481	15.0450
c/(Å)	7.3954	7.5370
β/°	119.738	120.047

Table S2 Fractional atomic coordinates for Ba_3P_5Cl (Space group = *C*2/*c*) used for the electronic structure calculations.

Atoms	*x*	*y*	*z*
Ba1	0.2769	0.0923	0.4346
Ba2	0	0.8154	¼
P1	0.3987	0.1088	0.0858
P2	0.1562	0.2997	0.1668
P3	0	0.2379	¼
Cl1	0	0	½

Table S3 Fractional atomic coordinates for Ba_3P_5Br (Space group = *C*2/*c*) used for the electronic structure calculations.

Atoms	*x*	*y*	*z*
Ba1	0.2835	0.0945	0.4390
Ba2	0	0.8110	¼
P1	0.3975	0.1075	0.0880
P2	0.1573	0.3004	0.1665
P3	0	0.2360	¼
Br1	0	0	½

Table S4 Fractional atomic coordinates for Ba_3P_5Cl (Space group = *Cc*) used for the electronic structure calculations.

Atoms	*x*	*y*	*z*
Ba1	0.2769	0.0923	0.6846
Ba2	0.2231	0.5923	0.3154
Ba3	0	0.1846	0
P1	0.3715	0.2280	0.0603
P2	0.3569	0.1190	0.2379
P3	0.0277	0.4283	0.0391
P4	0.1372	0.3551	0.3283
P5	0.0362	0.2538	0.4541
Cl1	0	0	1/4